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COMPLETE SPECIFICATION

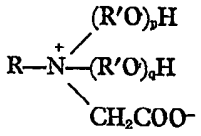
A Method of Preparing Photographic Light-Sensitive Elements

We, FUIJ SHASHIN FILM KABUSHIKI KAISHA, a Japanese Company, of No. 210, Nakanuma, Minami-Ashigara Machi, Ashigara-Kamigun, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates, generally, to a method of preparing photographic light-sensitive elements; more particularly the invention relates to a method of preparing a light-sensitive element in which an improved surface active agent is incorporated in a photographic coating composition, before its application, for improving the coating property thereof.

In producing photographic light-sensitive elements, a surface active agent is usually incorporated in photographic coating compositions such as photographic gelatino silver halide emulsions in order to promote uniform coating. For high speed applications in particular, the surface active agent thus incorporated must not reduce the photographic properties of the photographic light-sensitive element or the fastness of photographic images, in particular colour images, after processing the photographic light-sensitive element. Also it should improve the coating property or wetting property of the coating composition.

However, many conventionally known surface active agents have not sufficiently satisfied the above-mentioned requirements in the case of producing photographic light-sensitive elements. For example, an amphoteric surface active agent represented by the formula (A)



(A)

wherein R represents an alkyl group having more than 6 carbon atoms, R′ represents ethylene or propylene, and p+q is a positive integer larger than 5, produces an excellent improvement in the coating property of the coating composition containing it when the composition is applied to a support, but has faults. Since the presence of the surface active agent in a light-sensitive silver halide emulsion of a colour photographic light-sensitive element weakens the bleaching or silver-removing power in an oxidising bath during the developing process, silver images remain with colour images after processing and this reduces the clearness of the colours of colour photographs. Furthermore, since the surface active agent remaining after processing accelerates fading of colour images by heat and moisture, the life or stability of the colour photograph thus obtained is reduced.

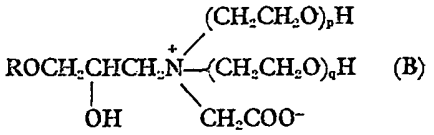
Moreover, in producing a colour photographic light-sensitive element using a hydrophobic oil-dispersion type coupler, an emulsified dispersion of the coupler prepared by finely dispersing the coupler in an aqueous medium together with an oily material by using an anionic surface active agent, is incorporated in a photographic silver halide emulsion. However, when in such a case, the surface active agent shown by the general formula (A) mentioned above is incorporated in the photographic silver halide emulsion, the colloidal stability of the dispersed coupler

particles is reduced; this causes aggregation of the coupler, tends to cause trouble during the production of the photographic light-sensitive elements, and lowers the transparency of the emulsion layer after development.

Thus, an object of the present invention is to provide an amphoteric surface active agent to be incorporated in a photographic coating composition for improving the coating property thereof without the aforesaid drawbacks.

Another object of this invention is to provide a method of preparing a photographic light-sensitive element, in particular a colour photographic light-sensitive element, by employing the aforesaid amphoteric surface active agent for improving the coating property of the photographic coating composition containing the agent on a support, without reducing the photographic properties of the photographic light-sensitive element and the fastness of colour images of the colour photographic light-sensitive element.

According to the present invention there is provided a method of preparing a photographic light-sensitive element by applying photographic coating compositions to a support, which method comprises incorporating in at least one coating composition before application a compound represented by the general formula (B):



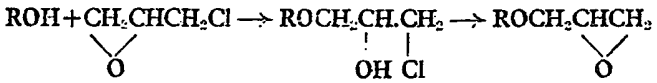
(B)

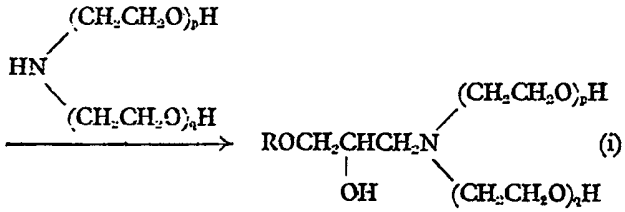
wherein R represents an alkyl group having 8—20 carbon atoms, and p and q each represents a positive integer.

Practical Examples of the amphoteric surface active agent used in the present invention are shown below:

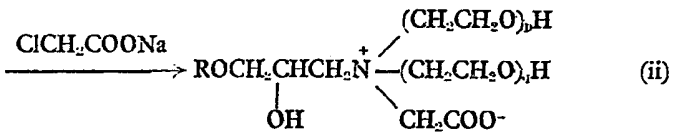
		R	p+q	
Compound	I	$C_{12}H_{25}$	2	(p=q)
„	II	$C_{12}H_{25}$	2	(p=q)
„	III	$C_{14}H_{29}$	5	
„	IV	$C_{14}H_{29}$	30	

These compounds may be prepared as follows:





(i)



(ii)

The synthesis (i) mentioned above may be conducted by the method described in "Kogyo Kagaku Zasshi (Journal of Industrial Chemistry)", Vol. 63, 595—600 (1960); and the synthesis (ii) may be conducted by the method described in "Kogyo Kagaku Zasshi", Vol. 60, 909 (1957).

The compound represented by the aforesaid general formula (B) may be incorporated in any suitable coating composition for a photographic light-sensitive element, but is preferably incorporated in a photographic silver halide emulsion. In this case, it is desirable to incorporate the surface active agent in the photographic silver halide emulsion in which the second ripening has been finished directly before coating. Furthermore, the surface active agents having the general formula (B) may be used together with other conventional surface active agents if necessary.

The optimum amount of the amphoteric surface active agent of the present invention to be incorporated varies in accordance with factors such as the kind of coating composition, the coating method, and the like, but in general the addition of 0.01—0.2% by weight of the surface active agent, based on the weight of the coating composition, gives the best results. This amount corresponds to 0.1—2.0 g. per one kg. of gelatin in the coating composition.

According to the process of this invention, a photographic emulsion containing the aforesaid surface active agent can be uniformly applied to a support at high speed and, at

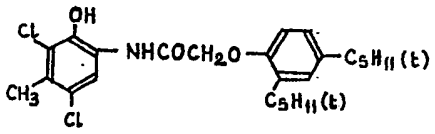
the same time, a photographic light-sensitive element having good photographic properties can be obtained; in particular, after developing a colour photographic light-sensitive element containing the surface active agent of this invention, colour images having a good fastness can be obtained.

Furthermore, since the amphoteric surface active agent used in this invention causes little undesirable interaction with other additives for the emulsion, the occurrence of trouble during the production of photographic light-sensitive elements can be reduced.

The invention will now be explained in detail by referring to the following Examples, in which Compounds I—IV are surface active agents as defined above to be used in the present invention, while Compound V represents a conventional surface active agent shown by the aforesaid general formula (A) in which R is $C_{14}H_{29}$, R' is C_2H_4, and p+q is 5.

EXAMPLE 1.

An emulsified dispersion prepared by dispersing a solution of 2.3 g. of a cyan coupler having the following formula:



in 5.0 ml. of tri-ortho-cresylphosphate ester in 40 ml. of an aqueous 10% gelatin solution containing 0.2 g. of sodium n-dodecylbenzene sulphonate, was added to 100 g. of a red-sensitive photographic emulsion containing 7 g. of gelatin and 5 g. of silver chlorobromide.

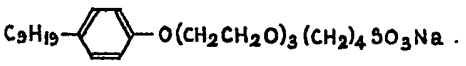
Into each of a series of samples of such emulsions were added 5 ml. of a 1% solution of Compounds I, II, III, IV, and V, respectively, and 3 ml. of a 3% acetone solution of triethylene phosphorus amide as a hardening agent. The coating compositions, thus prepared were applied to a triacetyl cellulose support followed by drying to provide light-sensitive films. Each light-sensitive film was red-exposed stepwise, developed in a colour developer containing 4 - amino - 3 - methyl - N,N - dimethylaniline hydrochloride as a developing agent, and then subjected to subsequent processing such as bleaching, fixing, water-washing, and drying, in a conventional manner, to provide a coloured sample. On the coloured samples thus obtained, the following fading tests were conducted; fading test (A) wherein the sample was maintained for 20 days under the conditions of 60°C. temperature and 75% relative humidity, the fading test (B) wherein the sample was maintained for 4 hours at 120°C. The results are shown in the following table in which the initial optical density of the cyan-coloured image was 2.0.

Surfactant	Fading % in Test A	Fading % in Test B
None (control)	3.0	24
Compound I	2.7	25
Compound II	2.5	21
Compound III	3.4	26
Compound IV	3.2	23
Compound V (comparative)	7.2	55

From the results, it was confirmed that by the incorporation of a conventional surface active agent V, fading of the coloured image was remarkably accelerated but no such marked acceleration of fading was observed when the surface active agents I, II, III, and IV of this invention were incorporated. Also, by the addition of the surface active agent of this invention, coloured images having a fastness similar to or higher than that of the control sample in which no surface active agent was added, were obtained.

EXAMPLE 2.

Into samples of a red-sensitive emulsion containing the coupler described in Example 1 were added 2.0 ml. of a 1% solution of each of Compounds I, II, III, and V, respectively, and 2.0 ml. of a 1% solution of a surface active agent having the following formula:



The coating compositions thus prepared were applied to triacetyl cellulose films at 35°C. and set at 5°C. To this coated emulsion layer, without drying, was applied at various coating speeds a coating composition prepared by adding 2 ml. of a 1% solution of a surface active agent, n-dodecylbenzene sulphonate, to 100 g. of a 2% gelatin solution. When the coating speed was increased over a definite figure, it became impossible to spread the second coating composition on the surface of the first emulsion layer. However, the upper limit of the coating speed was remarkably improved by adding Compounds I, II and III of this invention to the second coating composition as shown in the following table.

Surfactant	Limit of coating speed (m./min.)
None (control)	9
Compound I	50
Compound II	55
Compound III	50
Compound V (comparative)	42

EXAMPLE 3.

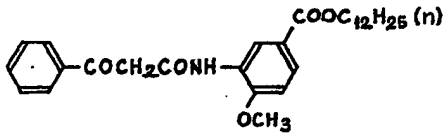
Into 10 ml. of a 7% gelatin solution was added 3.3 g. of the emulsified dispersion of the coupler described in Example 1, and to such samples of this mixture were added 5 ml. and 10 ml. of a 1% solution of Compounds II, IV, and V. The resulting mixtures were allowed to stand for 6 hours or 12 hours at 40°C., and thereafter applied to a glass plate in an amount corresponding to a dry thickness of 25 microns, followed by drying. Thereafter, the turbidity of the layers formed was measured, and the results are shown in the following table:

Surfactant	Amount	Turbidity (relative value) 0	6 hrs.	12 hrs.
None (control)	—	8.2	8.6	9.6
Compound II	5 ml.	10.2	10.2	13.0
"	10 ml.	10.2	11.7	13.7
Compound IV	5 ml.	8.0	9.2	12.0
"	10 ml.	17.9	18.3	18.9
Compound V	5 ml.	11.2	12.8	14.1
"	10 ml.	20.1	21.5	24.6

As is clear from the above results, when Compound II or IV of this invention was added, the colloidal stability of the coupler-containing emulsified dispersion was less reduced than in the case of adding conventional Compound V, and the emulsion layers formed in accordance with the present invention had good transparency.

EXAMPLE 4.

An emulsified dispersion prepared by dispersing a solution of 2.0 g. of a yellow coupler having the formula:



in 2.0 ml. of di-n-butylphthalic acid ester in 30 ml. of an aqueous 10% gelatin solution containing 0.2 g. of sodium n-dodecylbenzene sulphonate was added to 100 g. of a red-sensitive photographic emulsion containing 6 g. of gelatin and 6 g. of silver iodobromide.

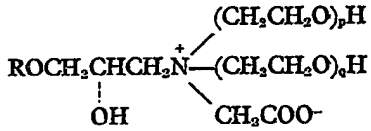
Samples of the emulsion thus prepared were mixed with 5 ml. of a 1% solution of Compounds I, II, and V, respectively, and 3 ml. of a 3% acetone solution of triethylene phosphorus amide. The mixtures were applied to triacetyl cellulose films, followed by drying, to provide light-sensitive films. Each light-sensitive film was then blue-exposed stepwise and processed as in Example 1 to provide a yellow image. The blue density D_b and red density D_r of the image were measured and the results are shown in the table below. The blue density D_b shows the strength of yellow coupling and the red density D_r shows the relative density of a silver image remained after processing.

Surfactant	D_b	D_r
Compound I	2.0	0.07
Compound II	2.0	0.05
Compound V	2.0	0.35

As shown in the results, in using Compounds I and II of this invention, the silver image was removed effectively by bleaching and clear yellow dye images were obtained while in the case of using the conventional Compound V, silver images remained to a considerable extent.

WHAT WE CLAIM IS:—

1. A method of preparing a photographic light-sensitive element by applying photographic coating compositions to a support, which method comprises incorporating in at least one coating composition before its application a compound represented by the general formula:



wherein R represents an alkyl group having 8—20 carbon atoms, and p and q each represents a positive integer.

2. A method as claimed in Claim 1, wherein R is $C_{12}H_{25}$ and p+q is 2.

3. A method as claimed in Claim 1, wherein R is $C_{14}H_{29}$ and p+q is 2.

4. A method as claimed in Claim 1, wherein R is $C_{14}H_{29}$ and p+q is 5.

5. A method as claimed in Claim 1, wherein R is $C_{14}H_{29}$ and p+q is 30.

6. A method as claimed in Claim 1, wherein the amount of said compound is 0.01—0.2% by weight based on the weight of the

coating composition in which it is incorporated.

7. A method as claimed in any preceding Claim, wherein the coating composition in which said compound is incorporated is a photographic silver halide emulsion.

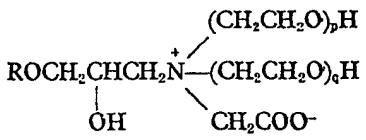
8. A method as claimed in any preceding Claim, wherein the coating composition in which said compound is incorporated is a colour photographic silver halide emulsion containing a coupler.

9. A method as claimed in Claim 8, wherein said compound is added to said silver halide emulsion after second ripening.

10. A method as claimed in claim 1 of preparing a photographic light-sensitive element, substantially as hereinbefore described with reference to any of the foregoing Examples.

11. A photographic light-sensitive element whenever prepared by a method according to any preceding Claim.

12. A coating composition for a photographic light-sensitive element, incorporating an amphoteric surface active agent represented by the general formula:



wherein R represents an alkyl group having 8—20 carbon atoms, and p and q each represents a positive integer.

13. A coating composition as claimed in claim 2 for a photographic light-sensitive element, substantially as hereinbefore described with reference to any of the foregoing Examples.

14. A photographic light-sensitive element comprising a support which carries thereon at least one photographic coating composition according to Claim 12 or Claim 13.

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